ADVANCES IN ION CHROMATOGRAPHY FOR MONITORING THE GOLD CYANIDATION PROCESS

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INTRODUCTION

During the gold cyanidation process, cyanide can be lost from the leachate by various chemical routes. Since cyanide is generally the most expensive reagent in this process, it is becoming increasingly important to monitor these cyanide losses. The products of these cyanide losses include base metal cyanide complexes, thiocyanate and cyanate.

The two most significant cyanicides in order of importance are sulfides and copper bearing minerals. The problems caused by cyanide soluble copper minerals are well known to the gold processing industry and have been reviewed by several authors (e.g. 1, 2). One particular facet of this problem concerns the effect of the CN:Cu mole ratio, R, on the gold leaching kinetics. In order to efficiently leach cupriferous ores, it is important that R is maintained at a level that allows sufficiently rapid leaching without excessive use of cyanide. An additional consideration when leaching cupriferous ores is the oxidation of cyanide by Cu(II) minerals, resulting in the formation of cyanate.

Ion chromatography (IC) has been successfully used for the determination of cyanide, metal cyanide complexes, thiocyanate and cyanate in leachates. Most of the important metal-cyanide complexes and thiocyanate can be determined by reverse phase ion interaction chromatography (e.g. 3, 4, 5, 6). Cyanide and cyanate are both unretained in the separation of the metal cyanide complexes and are not detectable as their respective anions. However, it has been possible to determine cyanide in this separation by either pre-column derivatisation with Ag to form $[Ag(CN)_2]^-$ (4) or post-column derivatisation with a selective colourimetric reaction to produce a visible dye (5) .There are no reactions suitable for the analogous pre or post column derivatisation of cyanate in the above separation of metal cyanide complexes. Cyanate has been determined separately on an anion exchange column (e.g. 7, 8, 9).

This paper presents two new IC techniques that enable the rapid determination of cyanate concentration and R in samples containing large concentrations of Cu(I)-cyanide complexes. Other metal cyanide complexes, in addition to Cu(I), can also be determined in conjunction with R, while other anions such as chloride and sulfate can be determined in conjunction with cyanate. The main aim of this work has been to solve some of the analytical problems associated with the cyanide leachates of cupriferous and pyritic ores.

ANALYSIS OF THIOCYANATE, METAL CYANIDE COMPLEXES AND THE CN:Cu MOLE RATIO

OVERVIEW

These analyses involve separation of cyanide, thiocyanate and the metal cyanide complexes on a reversed phase column using an ion interaction eluent. Thiocyanate and the metal cyanide complexes are detected with a photometric detector (UV detector), while cyanide is detected after post-column reaction (PCR) with a second photometric detector (PCR detector). The Cu(I) and Ag cyanide complexes and thiocyanate are also detected on the second photometric detector. A schematic of this instrument is shown in Figure 1. Chromatograms from both detectors from the analysis of a pyrite leach sample containing large concentrations of SCN, Cu(I) and Fe(II) (as the respective cyanide complexes) are shown in Figure 2.

INSTRUMENTAL CONDITIONS

HPLC Column : Waters Nova-Pak C-18, 3.9 x 150 mm or 3.9 x 50 mm

Injection volume : 1 - 10 µL (25 µL syringe) for Cu analysis; 50 - 100 µL (250 µL syringe) for Au analysis.

Eluent : 25 % acetonitrile, 10 mM tetrabutyl ammonium hydroxide, 10 mM KH_2PO_4, 5 mM H_2SO_4 and 4 - 8 ppm NaCN. Eluent pH was adjusted to 8.0 with NaOH. The eluent is kept at close to 0°C to minimise loss of acetonitrile and cyanide. Flow rate : 1.0 mL/min

UV detector : Programmable variable wavelength photometric detector. The detection wavelength can be varied during an analysis to enable changes in detection sensitivity as shown in Figure 3.

PCR detection :
Reagent #1 : 0.15 % N-chlorosuccinimide and 3.0 % succinimide in a 0.1 M succinate buffer, pH = 5.6.
Reagent #2 : 0.23 M isonicotinic acid, 15.6 mM barbituric acid, 2% Na_2EDTA, pH = 7.8
Both reagents are kept at close to 0°C.
PCR reagent flow rates : 0.1 mL/min (#1); 0.2 mL/min (#2)
Reaction coils : 1.5 m x 0.25 mm I.D. (#1) ; 5 m x 0.50 mm I.D. (#2). Reaction coils maintained at 40°C
Detection wavelength : 436 nm

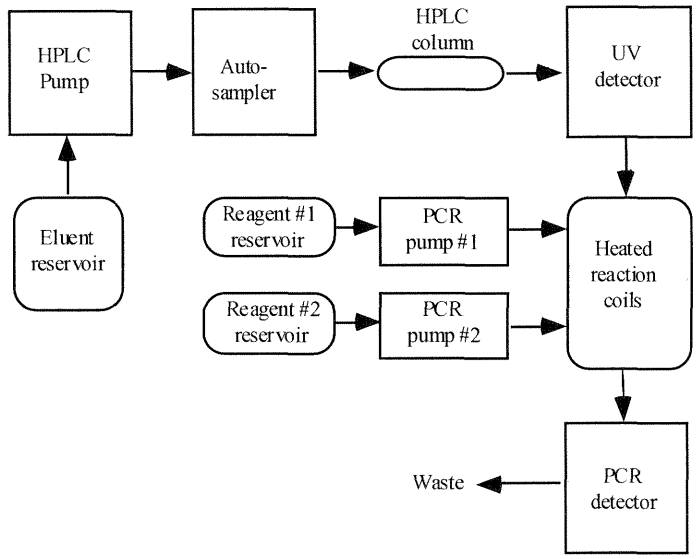


Figure 1 : Schematic of HPLC instrument for the analysis of metal cyanide complexes, thiocyanate and R.

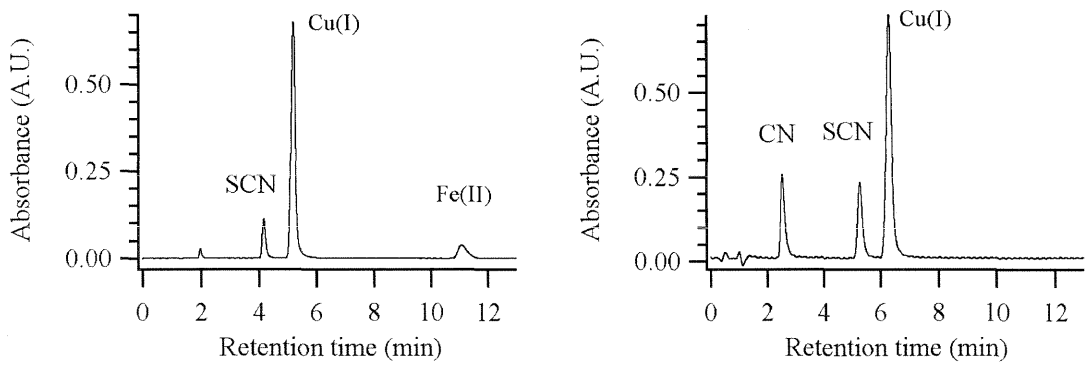


Figure 2 : Chromatograms from UV (left) and PCR (right) detectors.
Pyrite leach sample; Dilution factor : 7 ; Injection volume : 1 µL.
Concentrations : Cu(I)-cyanide (6653 ppm); SCN (4647 ppm); Fe(II) (300 ppm). R = 3.41

DETERMINATION OF THIOCYANATE AND THE METAL-CYANIDE COMPLEXES

Thiocyanate and the Cu(I) and Ag cyanide complexes can be determined from either the UV or PCR detector chromatograms. However, the precision obtained for thiocyanate from the PCR detector is considerably less than that obtained from the UV detector. The other metal cyanide complexes are determined from the UV detector chromatograms. All the calibration curves are linear. When the mass of Cu (as complexed Cu(I)-cyanide) injected onto the column is less than 2 µg, it is possible to perform the separation on a 5 cm column, enabling a rapid separation as shown in Figure 3.

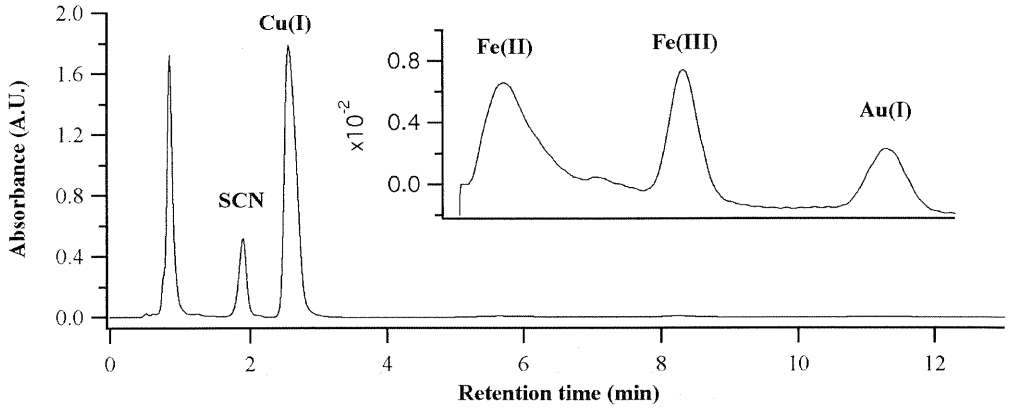


Figure 3 : Chromatogram from UV detector. Insert : Expanded chromatogram of minor, late eluting peaks. CIL sample; Undiluted sample; Injection volume : 50 µL
Detection wavelength changes : t = 0 min, λ = 205 nm; t = 2.2 min, λ = 245 nm, t = 5 min, λ = 205 nm.

DETERMINATION OF CN:Cu MOLE RATIO

The Cu(I)-cyanide complexes undergo partial dissociation during the chromatographic separation. The degree of this dissociation can be controlled by the addition of small quantities of cyanide to the eluent. For a given eluent, the R value of the eluted Cu(I)-cyanide peak remains constant, irrespective of the R value injected onto the HPLC column. Consequently, for a given Cu(I)-cyanide concentration, the cyanide peak area increases proportionally with R (10). The PCR conditions used in this method enable a linear relationship between R and the CN:Cu(I)-cyanide peak area ratio to be obtained for equimolar Cu(I)-cyanide standards as shown in Table 1. This relationship enables the HPLC instrument to be used for the determination of R in a sample following calibration with a series of Cu(I)-cyanide standards containing varying R values. By increasing the eluent cyanide concentration to 7 ppm NaCN, the calibration curve was applicable for Cu(I)-cyanide standards within the concentration range 15 ± 7.5 mM as shown in Figure 4.

Calibration drift due to the PCR detection system is eliminated by virtue of using the peak area ratio. The calibration drift that occurs is due to changing eluent conditions since the linear relationship varies with the eluent cyanide concentration as shown in Table 1. Under the controlled conditions used in this method, the calibration drift over a 2 week period was small, as shown in Table 2.

[NaCN] in eluent	Slope	Y-Intercept	X-Intercept	Linear regression coefficient
4 ppm	0.372	-1.006	2.70	0.998
5 ppm	0.372	-1.025	2.75	0.999
6 ppm	0.373	-1.042	2.84	0.999

Table 1 : Calibration parameters for CN:Cu mole ratio in eluents containing 4, 5 and 6 ppm NaCN. Calibrations for 10 µL injections of 1 mM Cu(I)-cyanide standards with R values ranging from 3.0 to 5.5

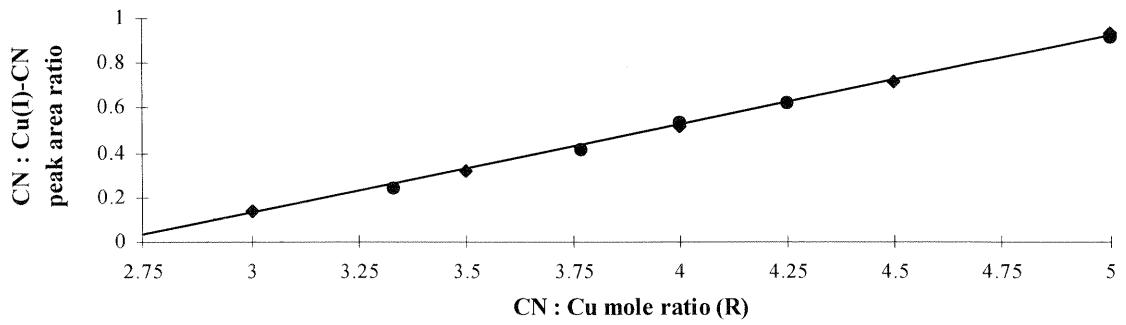


Figure 4 : Calibration curve for 1 µL injections of 15 mM Cu(I)-cyanide standards (•). Other points were for 7.5 - 22.5 mM Cu(I)-cyanide standards. Eluent [NaCN] = 7 ppm.

Calibration day and time	Peak area ratio for Cu(I)-cyanide standards					
	R = 3.0	R = 3.5	R = 4.0	R = 4.5	R = 5.0	R = 5.5
Day 1; 21:22	0.114	0.300	0.486	0.675	0.869	1.058
Day 2; 01:57	0.110	-	0.477	-	0.852	-
Day 7; 12:55	0.111	0.301	0.488	0.682	0.886	1.071
Day 7; 18:19	0.106	0.292	0.480	0.667	0.873	1.069
Day 7; 22:55	0.104	0.291	0.476	0.677	0.867	1.067
Day 11; 15:12	0.119	0.306	0.498	0.686	0.891	1.100
Day 11; 18:16	0.115	0.300	0.492	0.684	0.889	1.091
Day 11; 00:34	-	0.292	0.472	0.668	0.864	1.069
Day 11; 03:28	0.111	0.282	0.476	0.665	0.845	1.044
Day 13; 14 :10	0.120	0.304	0.502	0.691	0.904	1.096
Day 13; 20:01	0.114	0.306	0.491	0.694	0.896	1.087

Table 2 : Calibration drift for CN:Cu(I)-cyanide mole ratio. The same eluent compostion was used over this period. The eluent was freshly prepared every day. These eluents contained 4 ppm NaCN.

Analysis of samples containing CN:Cu mole ratios below calibration limit

It is obvious from examination of Table 1 that the minimum R value that can be determined varies from 2.70 to 2.84 in eluents containing from 4 to 6 ppm NaCN. Consequently, when the R value of a sample is below the point at which no cyanide peak is observed, it is necessary to perform a standard addition of NaCN to the sample. Depending on the nature of the sample, it may also be necessary to determine changes in other cyano species such as SCN^- and $[Fe(CN)_6]^{4-}$ after the NaCN addition. For example, it was found that the concentrations of these two species increased significantly after a NaCN addition to some pyrite leach samples with low R values (< 2.5). These increases were attributed to the presence of ultra-fine pyritic particulate matter in these samples. After the loss of cyanide to other species following the NaCN addition is taken into account, the value of R in the original sample can be calculated.

Justification of standard addition method for analysis of samples containing CN:Cu mole ratios below 3.0

The validity of this method was tested by performing standard additions of NaCN to pyrite leach samples containing R values greater than 3.0. The experimentally determined R values after the NaCN addition were within 5 % of the calculated values as shown in Table 3.

Sample number	[Cu] (ppm)	CN Cu mole ratio			Recovery (%)
		Before Std add	After Std addn	Calc from Std addn	
1	7040	3.10	3.97	3.07	96.4
2	6621	3.16	4.11	3.15	99.0
3	6324	3.16	4.19	3.19	102.9
4	5388	3.60	4.82	3.64	103.4
5	5306	3.31	3.31	3.37	105.2

Table 3 : Standard additions of NaCN to Pyrite leach samples with R > 3. The R value of each sample before and after the standard addition was determined. The R value of the original solution was then calculated from the value determined after the standard addition and compared to the value determined before the standard addition.

Comparison with standard techniques

Samples obtained from the cyanidation of cupriferous ores were analysed by the above IC technique and standard mine laboratory techniques. The copper concentration was determined by AAS, while the total cyanide was determined by acid distillation of the sample. The CN:Cu mole ratio was then determined from these two results. There was reasonably close agreement between the results obtained by IC and those obtained by the standard methods.

The major advantages of the IC technique are the rapid analysis time for determination of the CN:Cu mole ratio and the ability for this technique to be automated. An additional advantage is the reduced sample

dilution required for analysis of samples containing large concentrations of complexed Cu(I)-cyanide, thereby reducing potential errors. For example, by use of a 1 µL injection volume, the dilution required for the IC analysis of a sample containing 4000 ppm complexed Cu(I)-cyanide was 4, whereas a dilution factor of 100 was required for the AAS analysis.

ANALYSIS OF CYANATE IN SAMPLES CONTAINING METAL CYANIDE COMPLEXES

OVERVIEW

The process samples for which the methods described in this paper were developed contained large concentrations of cyanide, metal cyanide complexes (especially Cu(I) complexes), thiocyanate, chloride and sulfate. The typical range of chloride and sulfate concentrations in these samples was 1500 - 3000 ppm. For this reason, a high capacity anion exchange column was employed to reduce overloading effects due to chloride and sulfate.

The metal cyanide complexes have a very strong affinity with anion exchange resins (11). Consequently, these complexes would be very strongly retained on the analytical column resulting in reduced column efficiency and a drifting detection baseline. To avoid this, the complexed cyanides were removed from the samples prior to injection onto the analytical column with one of two procedures described below.

SEPARATION AND DETECTION OF CYANATE AND OTHER COMMON ANIONS

Since cyanate is a weakly retained species, eluting shortly after chloride, it is necessary to use a weak eluent to enable resolution of cyanate and chloride. Indirect UV detection was selected as it enabled the same detector to be used for both this analysis and for the separate analysis of metal cyanide complexes mentioned previously. This required the use of an aromatic carboxylic acid for the eluent since these are weak eluents with strong UV chromophores (12). Anthranilic acid (2-amino benzoic acid) was used for the eluent. The best separation and sensitivity was obtained with a 10 mM eluent at pH 7. This eluent pH enabled carbonate to be eluted early as HCO_3^- and prevented potential interference from cyanide, which was eluted unretained as HCN.

INSTRUMENTAL CONDITIONS

HPLC Column : Waters IC-Pak A HC, 4.6 x 150 mm
Injection volume : 2 µL (A 25 µL syringe enabled undiluted samples containing up to 5000 ppm Cu to be analysed with a precision of 1.4 % RSD, based on 5 replicate injections.)
Eluent : 10 mM anthranilic acid, pH 7. Flow rate : 1.0 mL/min
UV detector : Variable wavelength UV detector. Detection wavelength : 355 nm

METHODS FOR THE REMOVAL OF METAL CYANIDE COMPLEXES

1. Solid Phase Extraction (SPE) method

This method uses disposable SPE cartridges containing 500 mg of a quaternary amine strong anion exchanger (SAX) in the sulfate form. The SPE cartridges are conditioned prior to use. Solutions are pushed through the SPE cartridge at about 2 mL/min.

The following method enabled quantitative elution of cyanate off the cartridge and complete removal of Cu(I)-cyanide complexes from the sample :

(i) 200 mL of undiluted sample is placed into the SPE cartridge and then slowly pushed onto the SAX sorbent.

(ii) 2.2 mL of 15 mM Na_2SO_4 is then placed into SPE cartridge and also slowly pushed onto the SAX sorbent.

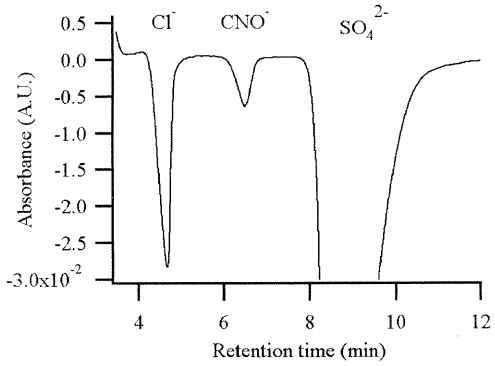
(iii) The effluent (~2.4 mL) from the SPE cartridge is placed directly into an autosampler vial, from which 50 µL is injected onto the HPLC column.

A typical chromatogram using this method is shown in Figure 5. Note the vey large sulfate peak.

2. On-line method

This method uses a column switching valve and a guard column to enable the on-line removal of the metal cyanide complexes as shown in Figure 6. Immediatedly after injection of a sample, the metal cyanide complexes are retained on the guard column, while cyanate is rapidly eluted off the guard column, together with other common anions for analysis on the analytical column as shown in Figure 7. The metal cyanide

complexes are then backflushed off the guard column when the column switching valve is turned 30 seconds after injection of the sample. A second pump is used to backflush the guard column with the same eluent used for the analytical column.



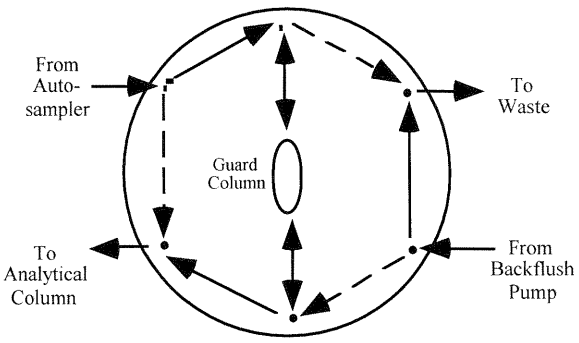


Figure 5 (Left) : Analysis of cyanate after removal of the metal cyanide complexes with SPE method.
Figure 6 : (Right) Switching valve configuration for the on-line removal of metal cyanide complexes. (→)Flow direction after injection of sample. (Dashed →) Flow direction during backflush of guard column.

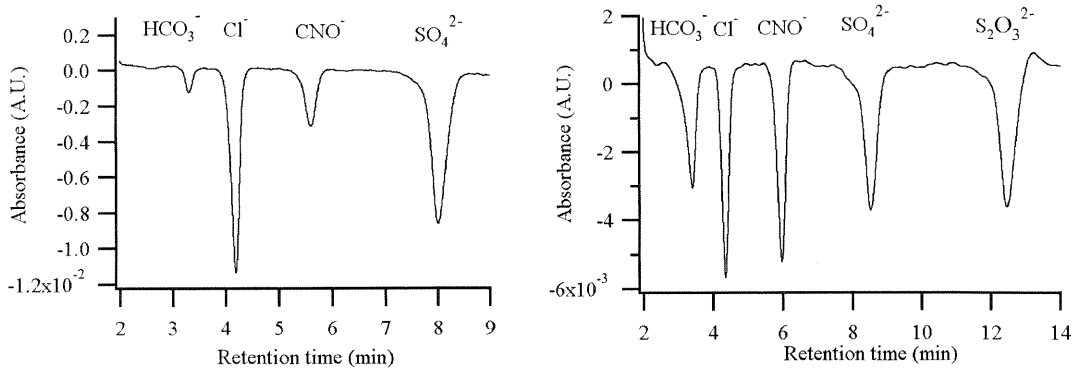


Figure 7 Analysis of samples after on-line removal of metal cyanide complexes. Samples from cyanidation of cupriferous ores (Left) and pyrite leachate (Right). The anion concentrations (in ppm) in these samples were : [Cl^-] = 965 (L), 648 (R); [CNO^-] = 502 (L), 1012 (R); [SO_4^{2-}] = 2227 (L), 1348 (R).

Verification of on-line method for the removal of Cu(I)-cyanide complexes

The reaction between Cu(II) and cyanide was used as a test for the on-line removal of Cu(I)-cyanide complexes and subsequent IC analysis for cyanate. In this test, solid $CuCl_2$ (2.5 mmol) was dissolved in an alkaline solution containing excess NaCN (12.5 mmol). The cyanate concentration in the three replicate injections was found to be 209 ± 1 ppm. The expected cyanate concentration was 210 ppm.

Comparison of the two methods for the removal of metal cyanide complexes

The advantage of the SPE method is that less equipment is required since only a conventional HPLC instrument consisting of a single pump, injector and detector is used. The on-line method requires a column switching valve and a second pump in addition to the previous HPLC instrument.

However, the operational costs are considerably greater with the SPE method due to the operator time required for sample preparation and the use of one SPE cartridge per sample. An additional benefit of the on-line method is the determination of other common anions in the leachate, in addition to cyanate, as shown in Figure 7.

Comparson of on-line IC method with standard wet chemical (Kjdeldahl) method

Some samples from the cyanidation of cupriferous ores were analysed for cyanate using both the on-line IC method and the wet chemical Kjeldahl method. The Cu concentration (as the complexed Cu(I)-cyanide) in these samples varied from 5000 - 6000 ppm and the CN:Cu mole ratios were between 3 and 4. There was a significant discrepancy between the two methods, with the IC method reporting a considerably lower

concentration as shown in Table 4. This difference was attributed to the formation of cyanate in the acid hydrolysis step of the Kjeldahl method in the presence of large concentrations of complexed Cu(I)-cyanide.

Sample	[OCN^-] / ppm	
	Kjeldahl method	IC method
#1	210	113
#2	235	161
#3	340	238
#4	530	294
#5	420	257

Table 4 : Comparison of cyanate analyses using the Kjeldahl and IC methods. The samples contained large concentrations of complexed Cu(I)-cyanide.

CONCLUSIONS

The two new IC techniques reported in this paper allow the rapid and reliable determination of all the cyano species found in leachates of cupriferous and pyritic ores. The CN:Cu mole ratio and the concentrations of thiocyante and the metal cyanide complexes are determined with the first technique, while the cyanate concentration is determined with the second technique. These analyses allow the total cyanide concentration distributed between the various cyano species to be determined. The alternative classical techniques are considerably more time consuming than these IC techniques and, in the case of cyanate, prone to interference from large concentrations of complexed Cu(I)-cyanide.

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